Inorganic Chemistry 2016 vol.55 N20, pages 10692-10700

Structure-Property Relationships in α-, β′-, and γ-Modifications of $Mn_3(PO_4)_2$

Volkova O., Shvanskaya L., Ovchenkov E., Zvereva E., Volkov A., Chareev D., Molla K., Rahaman B., Saha-Dasgupta T., Vasiliev A.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2016 American Chemical Society.The manganese orthophosphate, $Mn_3(PO_4)_2$, is characterized by the rich variety of polymorphous modifications, α-, β′-, and γ-phases, crystallized in monoclinic $P2_1/c$ ($P2_1/n$) space group type with unit cell volume ratios of 2:6:1. The crystal structures of these phases are constituted by three-dimensional framework of corner- and edge-sharing [MnO_5] and [MnO_6] polyhedra strengthened by [PO_4] tetrahedra. All compounds experience long-range antiferromagnetic order at Neel temperature T_N = 21.9 K (α-phase), 12.3 K (β′-phase), and 13.3 K (γ-phase). Additionally, second magnetic phase transition takes place at $T*$ = 10.3 K in β′-phase. The magnetization curves of α- and β′-modifications evidence spin-floplike features at B = 1.9 and 3.7 T, while the γ-$Mn_3(PO_4)_2$ stands out for an extended one-third magnetization plateau stabilized in the range of magnetic field B = 7.5-23.5 T. The first-principles calculations define the main paths of superexchange interaction between Mn spins in these polymorphs. The spin model for α-phase is found to be characterized by collection of uniform and alternating chains, which are coupled in all three directions. The strongest magnetic exchange interaction in γ-phase emphasizes the trimer units, which make chains that are in turn weakly coupled to each other. The spin model of β′-phase turns out to be more complex compared to α- or γ-phase. It shows complex chain structures involving exchange interactions between Mn2 (Mn2′, Mn2″) and Mn3 (Mn3′, Mn3″). These chains interact through exchanges involving Mn1 (Mn1′, Mn1″) spins.

http://dx.doi.org/10.1021/acs.inorgchem.6b01942